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(54) COMPOSITION AND METHOD FOR INHIBITING CORROSION OR WHITE RUST FORMATION ON METAL COMPONENTS IN THE WATER SYSTEM

ZUSAMMENSETZUNG UND VERFAHREN ZUR INHIBIERUNG VON KORROSION ODER WEISSROSTBILDUNG AN METALLKOMPONENTEN IM WASSERSYSTEM

COMPOSITION ET MÉTHODE POUR INHIBER LA CORROSION OU LA FORMATION DE ROUILLE BLANCHE SUR LES COMPOSANTS MÉTALLIQUES DANS LE SYSTÈME D'EAU

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Description

Background of the Invention

1. Field of the Invention

[0001] This invention relates to a treatment composition and method for inhibiting corrosion or white rust on metal components in water systems. This invention is particularly useful in the corrosive environments found in low LSI (Langelier Saturation Index) water systems, such as open recirculating systems, closed loop cooling or heating systems, and boilers.

2. Description of Related Art

[0002] Various water treatment compositions are used to reduce corrosion, mineral scale, and white rust formation on metal components in contact with an aqueous solution in water systems such as open recirculating systems, closed loop cooling or heating systems, cooling towers and boilers, and help protect the metal components of these systems. The metals typically used in these water systems include ferrous metals, including galvanized steel, aluminum and its alloys, copper and its alloys, lead, and solder. Many known corrosion inhibitors contain regulated toxic metals, such as zinc, chromate, and molybdate, which are harmful to the environment and increase the costs. Zinc is typically used as corrosion inhibitor in water systems with highly corrosive water (low LSI). However its usage is undesirable due to toxicity issues and its use faces regulations in some locations. Tin has also been used as a non-toxic alternative to zinc, but it is more expensive.

[0003] The performance of many known corrosion inhibitors is also negatively impacted by the use of biocides, which are frequently used in water systems to control the growth of microorganisms. The use of polyaspartic acid and a single phosphonic acid are disclosed in U.S. Patent No. 5,523,023 as effective in inhibiting corrosion, even in the presence of a biocide when the phosphonic acid is 2-phosphonobutane-1,2,4-tricarboxylic acid (PBTC). The preferred phosphonic acid in the ’023 patent is PBTC, but other phosphonic acids, including 1-hydroxyethane 1,1-disphosphonic acid and hydroxyphosphonoacetic acid (HPA) are also mentioned as suitable. The corrosion rate results shown in the ’023 patent based on the use of polyaspartic acid and PBTC are better than other corrosion inhibitors, but there is still a need for even greater corrosion inhibition, particularly in the presence of biocides.

[0004] Currently utilized solutions for white rust prevention include passivating the metal surfaces with zinc carbonate and control of water chemistry to reduce potential for white rust formation. Known treatments include the use of inorganic phosphates, thiocarbamates, organo-phosphorous compounds and tannins. For example, U.S. Patent Nos. 5,407,597 and 6,468,470 disclose compositions comprising organophosphorus compounds (including PBTC), an alkali metal salt of molybdenum, titanium, tungsten, or vanadium, and either a carbamate compound or a tannin compound. U.S. Patent No. 6,183,649 discloses a white-rust treatment composition comprising PBTC, sodium polyacrylate, sodium tolytriazole, an alkali metal molybdate, and an alkali metal bromide for treating circulating water systems. The ’649 patent also discloses the addition of a 1.5% aqueous solution of decyl thioethyletheramine (DTEA) at a rate of 11,340 g/3.79 m^3 (25lb/1,000 gallons) of water/week to the circulating water system prior to adding the white rust treatment composition at a rate of 600 ppm per cycle for ten cycles of recirculation after addition of the DTEA.

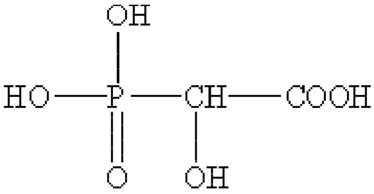
[0005] US 5,407,597 relates to a white rust inhibiting composition and method of inhibiting white rust for evaporative water coolers, wherein composition includes in combination a blend of one or more organophosphorus compounds, one or more carbamate compounds, and one or more water soluble metal compounds. US 6,468,470 discloses a white rust inhibiting composition and method of inhibiting white rust for evaporative water coolers, wherein composition includes, in combination, a blend of one or more organophosphorus compounds, one or more tannin compounds, and one or more water soluble metal compounds. CN 103 319 010 relates to a scale and corrosion inhibitor, comprising organic phosphonate, an inorganic scale and corrosion inhibition component, a carboxylic acid containing copolymer, zinc salt, a heterocyclic compound and a fluorescence tracing component. CN 1 273 393 C relates to a composite scale and corrosion inhibitor, which comprises organic phosphonic acid, polyaspartic acid containing phosphonic acid groups, copolymer containing carboxylic acid groups and zinc salt, and a copper material corrosion inhibitor. CN 102 838 216 discloses a treatment composition containing 35-40% of polyaspartic acid, 18-28% PBTC, DCYTA, and phosphonoglycolic acid. CN 1 743 282 discloses compositions comprising PBTC and/or hydroxyphosphonoacetic acid with amino acid based polymer and/or polyexpoxysuccinic acid and a carboxylic acid containing polymer. For corrosion inhibition, zinc salts should be included in the composition.

[0006] There is a need for an effective corrosion inhibitor and an effective white rust inhibitor composition and method that are more environmentally friendly and capable of adequately performing in conjunction with biocides. There is also a need for a single treatment composition and method that will address both corrosion and white rust without the need for separate treatments, which may negatively interact with each other.

SUMMARY OF THE INVENTION

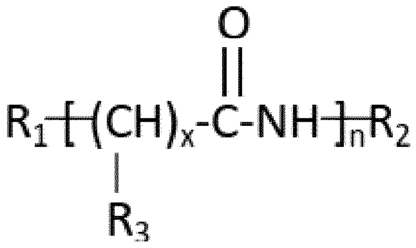
[0007] The present invention relates to a method of treating water systems to inhibit corrosion or white rust formation on metal components in the water system, the method comprising adding to the water system having a volume of water: an amino-acid based polymer or its water soluble salt; a first phosphonic acid or its water soluble salt; and a second phosphonic acid or its water soluble salt; and wherein the first phosphonic acid is hydroxyphosphonoacetic acid or its water soluble salt; wherein the adding step provides an active concentration in the volume of water of (1) 3 ppm - 50 ppm of the amino-acid based polymer or its water soluble salt, (2) 3 ppm - 50 ppm ppm of the hydroxyphosphonoacetic acid or its water soluble salt, and (3) 2 ppm - 20 ppm of the second phosphonic acid or its water soluble salt; and wherein no zinc, chromate, molybdate, or tin are added to the water in the water system. The present invention further relates to a composition for inhibiting corrosion or white rust on metal components in water systems comprising a volume of water, the composition comprising: 2-15% by weight of an amino-acid based polymer or its water soluble salt; 2-10% by weight of hydroxyphosphonoacetic acid or its water soluble salt; 2-10% by weight of a second phosphonic acid or its water soluble salt; and one or more of a neutralizing amine, chlorine stabilizer, a scale inhibitor, a dispersion agent, another corrosion inhibitor, chelants, an azole corrosion inhibitor, and a fluorescent dye tracer; and wherein the composition does not include zinc, chromate, molybdate or tin. Preferred embodiments are described in the subclaims.

[0008] According to the invention, an improved corrosion inhibitor and white rust inhibitor composition comprises an amino-acid based polymer (AAP), hydroxyphosphonoacetic acid (HPA) or its water soluble salt, and another phosphonic acid or its water soluble salt. Hydroxyphosphonoacetic acid has the following general structure:



$$HO-\underset{\displaystyle \overset{\|}{O}}{\overset{\displaystyle OH}{\overset{|}{P}}}-\underset{\displaystyle OH}{\underset{|}{CH}}-COOH$$

[0009] Most preferably, the amino-acid based polymer is polyaspartic acid or its water soluble salt, but other compounds such as polyglycine acid, polyglutamic acid and their salts may also be used. Most preferably, the amino acid based polymer has the following formula:



$$R_1 - [\underset{\displaystyle R_3}{\underset{|}{(CH)_x}} - \overset{\displaystyle O}{\overset{\|}{C}} - NH]_n R_2$$

where R1 = H, R2=OH, and R3=COOH and x=1 for polyaspartic acid. Most preferably, the other phosphonic acid is a phosphonocarboxylic acid or any organic phosphonate may also be used. Most preferably, the phosphonocarboxylic acid is 1-hydroxyethane-1,1-diphosphonic acid (HEDP) or 2-phosphonobutene-1,2,4-tricarboxylic acid (PBTC) or phosphonosuccinic acid. Preferably the weight ratio of AAP to HPA in the inhibitor composition is 90:10 to 10:90 and the ratio of combined AAP and HPA to other phosphonic acid is in the range of 90:10 to 60:40. More preferably, the weight ratio range of AAP to HPA in the inhibitor composition is 80:20 to 80:20 and the ratio of combined AAP and HPA to other phosphonic acid is 80:20 to 70:30.

[0010] The composition according to the invention is all organic and does not contain regulated metals such as zinc, chromate, and molybdate and its performance is not affected by addition of biocides. The composition according to the invention does not contain tin either.

[0011] It was previously known to use both HPA and AAP, such as polyaspartic acid, separately as corrosion inhibitors. It was also disclosed in the '023 patent that AAP could be used together with phosphonocarboxylic acid to inhibit corrosion, but it was not previously known to use AAP and HPA together along with another phosphonic acid, preferably a phosphonocarboxylic acid, or an organic phosphonate to inhibit corrosion.

[0012] When added to the water in the water system being treated, a preferred composition according to the invention yields at least 3 ppm active AAP, at least 3 ppm active HPA, and at least 2 ppm of the other phosphonic acid. When added to the water in the water system being treated, the composition yields 3 ppm-50 ppm AAP, 3 ppm-50 ppm HPA, and 2 ppm-20 ppm of the other phosphonic acid and preferably between 5ppm-30ppm AAP 3ppm-20ppm HPA, and 2 ppm-10 ppm of the other phosphonic acid. Additionally, the combined total of the three components of a preferred composition yields at least 8 ppm active corrosion inhibitors when added to the water being treated. These ingredients have the unexpected synergistic effect of improved corrosion inhibition without requiring the use of toxic metals and without being adversely impacted by biocides.

[0013] In addition to unexpected and synergistic effect of the inhibitor composition on ferrous metal corrosion inhibition in low LSI water, the same composition also has a positive effect on preventing formation of white rust on galvanized steel. Galvanized steel consists of a thin coating of zinc fused to a steel substrate. White rust is a rapid, localized corrosion attack on zinc that usually appears as a voluminous white deposit. This rapid corrosion can completely remove zinc in a localized area with the resultant reduction in equipment life. Neither hydroxyphosphonoacetic acid nor amino-acid based polymers, such as polyaspartic acid, alone or in combination, has been previously utilized in commercial products for white rust prevention. Without being bound by theory, it is believed that the compositions according to the invention may be forming a protective layer on the surface of galvanized steel and reduce white rust formation. For treating white rust according to the invention, it is preferred to use hydroxyphosphonoacetic acid, an amino-acid based polymer, and another phosphonic acid in the amounts indicated above for inhibiting corrosion (both weight ratios and concentrations when added to the water in the water system being treated), but it has also been found that the use of an amino-acid based polymer without hydroxyphosphonoacetic or the other phosphonic acid is beneficial at inhibiting white rust.

[0014] The compositions for inhibiting corrosion or white rust also comprise one or more of the following ingredients: a neutralizing amine, chlorine stabilizer, such as monoethanol amine (MEA); a scale inhibitor and dispersion agent, such as polycarboxylate polymer and/or carboxylate/sulfonate functional copolymers (typical examples: polyacryclic acid (PAA), polymethacrylic acid (PMAA), polymaleic acid (PMA), and copolymers of acrylic acid sulfonated monomers, such as AA/AMPS); other scale and corrosion inhibitors, chelant agents; azole corrosion inhibitors, such as benzotriazole, alkylbenzotriazole (tolyltriazole); and/or a fluorescent dye tracer, such as 1,3,6,8-Pyrenetetrasulfonic acid tetrasodium salt (PTSA). The overall composition comprises 2%-15% (by weight) of an amino-acid based polymer (such as polyaspartic acid), 2% to 10% (by weight) of hydroxyphosphonoacetic acid, and 2% to 10% (by weight) of another phosphonic acid.

[0015] According to one preferred method of preventing corrosion of metal components and/or white rust on galvanized steel components in a water system, a treatment composition according to the preferred embodiments of invention as described above is added to the water system. For a composition combining one or more of the AAP, HPA, and another phosphonic acid as described above, a preferred method comprises feeding the composition into the water at an effective feed rate of 20ppm - 600 ppm, or more preferably 100 - 300ppm, of treatment composition, depending on the treated water chemistry and the amount of optional components in the treatment composition. Preferably, a sufficient amount of treatment composition is added to the water system to provide effective active amounts of one or more of the three treatment components (depending on whether corrosion or white rust is being treated or both) of at least 3 ppm AAP, at least 3 ppm HPA, and at least 2 ppm of another phosphonic acid, each as concentrations when added to the volume of water in the water system being treated. The treatment composition is added in a sufficient amount to provide effective active amounts one or more of the components of between 3 ppm - 50 ppm AAP, between 3pm - 50 ppm HPA, and between 2 ppm - 20 ppm of another phosphonic acid when added to the water in the water system. Preferably, these effective active amounts are 5ppm - 30 ppm AAP, 3 ppm - 20 ppm HPA, and 2 ppm - 10 ppm other phosphonic acid when added to the water in the water system.

BRIEF DESCRIPTION OF THE DRAWINGS

[0016] The composition and method of the invention are further described and explained in relation to the following figures wherein:

FIG. 1 contains photographs showing corrosion levels on steel coupons after spinner tests at flow rates of 0.91 m/sec (3ft/sec) and 1.52 m/sec (5ft/sec);

FIG. 2 contains photographs showing corrosion levels on steel coupons after spinner tests run in presence of biocide at flow rates of 0.91 m/sec (3ft/sec) and 1.52 m/sec (5 ft/sec);

FIG. 3 contains photographs showing corrosion levels on steel coupons after spinner tests at a flow rate of 0.91 m/sec (3ft/sec); and

FIG. 4 contains photographs showing white rust levels on galvanized coupons after spinner tests.

DESCRIPTION OF PREFERRED EMBODIMENTS

[0017] Several lab tests were run to test the effectiveness of various compositions according to the invention. Compositions according to the invention were evaluated using spinner tests to simulate flowing water over metal components in a water system. Each spinner test set-up comprises a stainless steel container of water with four metal coupons (mild steel coupons (C1010) and copper coupons (CDA 11) were used) suspended in the water in each container from holders hanging from a rotating shaft. The shaft rotates the coupons in the water in the stainless steel container at 147 rotations/min, representing a flow rate of 0.91-1.52 m/s (3-5 ft/s), depending on coupon distance from center of the rotating shaft. The initial volume of water used in each spinner test was characteristic of corrosive, low hardness water typically found in water systems. The water used had the characteristics shown in Table 1 below.

Table 1. Low hardness, corrosive water used in Spinner test experiments. 1cps is equal to 1mPa.s

Characteristic	Value	Unit
pH	8 to 8.5	
Conductivity	220	cP
Ca Hardness	30	ppm, (as CaCO3)
Mg Hardness	10	ppm, (as CaCO3)
Chlorides, Total	25	ppm Cl
M Alkalinity	30	ppm, (as CaCO3)
Sulfate, Total	28	ppm, as SO4

[0018] During each spinner test the water is aerated and maintained at constant temperature of 49°C (120F) and constant volume (any evaporation is compensated with automatic addition of deionized water when water level drops below sensor level). Standard test duration is 48 hours.

[0019] Using the spinner test set-up, compositions according to preferred embodiments of the invention (Example Nos. 1-3 including AAP, HPA, and another phosphonic acid - HEDP) without any added zinc or tin (as shown in Table 2) were compared to compositions using only zinc (Comp. Ex. 4), only tin (Comp. Ex. 5), only AAP (Comp. Ex. 6), only HPA (Comp. Ex. 7), HPA combined with tin (Comp. Ex. 8), and AAP combined with tin (Comp. Ex. 9) (all as shown in Table 3) as the primary inhibitor(s). The ppm concentrations of the various treatments are concentrations when added to the volume of water in the spinner test container. The compositions with zinc or tin were for comparison to those without. Zinc is typically used as corrosion inhibitor in water systems with highly corrosive water (low LSI). However its usage is undesirable due to toxicity issues and its use face regulations in some locations. Tin has been promoted and patented as a non-toxic alternative to zinc, but it is more expensive. In addition to the primary corrosion inhibitor components listed in Tables 2 and 3, all of the tests were carried out in the presence 4 ppm active AA/AMPS copolymer and 4 ppm active TTA. These ingredients were added to the water in each spinner test set-up to provide those concentration levels. The corrosion and pitting level for mild steel coupons after spinner tests in presence of different inhibitors are presented in Figure 1.

Table 2. Corrosion inhibitor compositions according to the invention

Inhibitor	Unit	Example 1	Example 2	Example 3
AAP (amino acid based polymer - specifically Baypure DS 100/40, which is a sodium salt of polyaspartic acid; water solution containing about 40% of salt)	ppm active*	7.5	5.2	5.2
HPA (hydroxyphosphonoacetic acid)	ppm active	2.5	5.0	5.0
HEDP	ppm active	3	3	3
MEA	ppm	0.25	1.0	
Zn (zinc)	ppm active	N/A	N/A	N/A
Sn (tin)	ppm active	N/A	N/a	N/A
*ppm active refers to the amount of active raw material, in contrast to ppm which refers to the weight of raw material in mg/L. For example, HPA is commercially available as a 50% water solution, so adding 10 ppm raw material will provide 5 ppm active HPA.				

Table 3. Corrosion inhibitor compositions - Comparative

Examples							
Inhibitor	Unit	Comp. Ex 4	Comp. Ex 5	Comp. Ex 6	Comp Ex 7	Comp. Ex 8	Comp. Ex 9
AAP	ppm active			15			7.5
HPA	ppm active				5	5	
HEDP	ppm active	3	3	3	3	3	3
MEA	ppm						
Zn	ppm active	1					
Sn	ppm active		1			1	0.5

[0020] Spinner tests were run with each composition at a flow rate equivalent to 0.91 m/second (3ft/second) and at a flow rate equivalent to 1.52 m/second (5ft/second). A control test, without any treatment was also carried out for comparison. FIG. 1 shows photographs of a representative mild steel coupon after each spinner test with the control and with Example Composition Nos. 1-9. The amount of corrosion and pitting on the coupons is shown in the photographs. As can be seen, the control coupons show extensive corrosion (dark areas on photographs). The coupons used with compositions according to preferred embodiments of the invention (Ex. Nos. 2-3) show little, if any, corrosion or pitting (very few dark areas on photographs). The coupons used with Ex. No. 1, which contains all three components according to a preferred embodiment of the invention for corrosion inhibition, but only contains 2.5 ppm HPA (less than the more preferred amount of at least 3 ppm), shows improved results over the control and the comparative examples (Comp. Nos. 4-9), but shows slightly more corrosion than Ex. Nos. 2-3, where 5 ppm of HPA was used. The coupons used with the comparative compositions (Comp. Nos. 4-9) are significantly better than the control, but do show evidence of corrosion and pitting that is greater than with Ex. Nos. 1-3. Based on the results, it appears that the combination of AAP, HPA, and another phosphonic acid (in these examples, HEDP) interact synergistically to provide improved corrosion control, without requiring the use of zinc, tin or other regulated metals.

[0021] Some prior art water treatment corrosion inhibition compositions do not provide effective protection when oxidizing biocides are used in the same system to prevent biological growth. The most widely used oxidizing biocides are chlorine and stabilized bromine. Additional spinner corrosion tests were carried out using Example compositions Nos. 2 and 3 compared to comparative Example compositions Nos. 4 (zinc only) and 7 (HPA only) in the presence of a stabilized bromine biocide composition (commercially available as Chem-Aqua 42171). Example compositions 4 and 7 were selected because they showed the best results in the spinner tests of the comparative examples. Both Comp. Ex. Nos. 4 and 7 perform fairly well in low LSI water, but as discussed below, significantly worse when biocide is added. Also, Comp. Ex. No. 4 is based on zinc, which is undesirable to use due to toxicity concerns. As with the prior tests, these tests were carried out in presence 4 ppm active AA/AMPS copolymer and 4 ppm active TTA. A slug dose of 40ppm of biocide was added at the beginning of each spinner test (after the corrosion inhibition composition was added and the test started) to yield about 1ppm FHR (free halogen residue).

[0022] FIG. 2 shows photographs of a representative mild steel coupon after each spinner test with the Example Compositions in the presence of biocide. As can be seen, the coupons used with compositions according to preferred embodiments of the invention (Ex. Nos. 2-3) show little, if any, corrosion or pitting, indicating that the functionality of preferred compositions according to the invention is not negatively affected by a biocide. The coupons used with the comparative compositions (Comp. Ex. Nos. 4 and 7) show substantially more corrosion than with Ex. Nos. 2-3. It is noted that Comp. No. 7 was the use of HPA and HEDP, without any AAP, which showed good results without biocide, but significantly more corrosion occurred when a biocide was added. The comparative composition having AAP and HEDP, without any HPA, (Comp. Ex. No. 6) did so poorly without biocide (Fig. 1 above) that it was not tested with biocide because the results would be expected to be even worse than in FIG. 1. Based on the results, it appears that the combination of AAP, HPA, and another phosphonic acid together interact synergistically to provide improved corrosion control even in the presence of a biocide and show improved results over the use of HPA alone.

[0023] Corrosion rates for the mild steel coupons were also measured and calculated from weight loss of the coupons. The results of both the spinner tests without added biocide and with added biocide are summarized in Table 4. Information on corrosion mode, particularly the presence of pitting (which is important in many applications and some corrosion inhibitors, including HPA used alone, are known to be poor protectors against pitting), is also included in Table 4. Most preferably, corrosion inhibitor compositions according to the embodiments of the invention achieve corrosion rates of 0.07 mm/yr (3 MPY) or less for corrosion, even in the presence of a biocide.

Table 4. Corrosion Rates form spinner test experiments

Mild Steel Coupon Corrosion Rate, mm/yr (MPY [mil/yr])						
	Low Hardness Water			Low Hardness Water + Biocide		
Test	0.91 m/sec (3ft/sec)	1.52 m/sec (5ft/sec)	Pitting Scale	0.91 m/sec (3ft/sec)	1.52 m/sec (5ft/sec)	Pitting
Control	9.40 (370)	6.17 (243)	N/A			
Example 1	0.07 (2.7)	0.06 (2.5)	None			
Example 2	0.07 (2.9)	0.06 (2.4)	None	0.06 (2.2)	0.05 (2.0)	None
Example 3	0.06 (2.5)	0.06 (2.5)	None	0.07 (2.7)	0.06 (2.4)	None
Comp. Ex 4	0.07 (2.7)	0.07 (2.7)	Limited	0.20 (8.0)	0.28 (11)	Sever pitting
Comp. Ex 5	0.10 (4.0)	0.12 (4.6)	Pitting			
Comp. Ex 6	0.35 (13.6)	0.21 (8.2)	Severe pitting			
Comp. Ex 7	0.07 (2.6)	0.08 (3.2)	Limited	0.16 (6.4)	0.14 (5.7)	Severe pitting
Comp. Ex 8	0.10 (3.9)	0.13 (5.2)	Pitting			
Comp. Ex 9	0.10 (3.8)	0.08 (3.2)	Sever pitting			
Pitting scale description: None = no pitting observed Limited = few (1-5) pitts per coupon, usually very shallow Pitting = significant number of pits on coupons (5-50) Sever pitting = a large number of pits (> 50), usually dipper and larger						

[0024] Compositions according to preferred embodiments of the invention contain organic phosphate from the HPA and from the other phosphonic acid used in these examples (HEDP). In the presence of a biocide, the organic phosphate is often reverted to orthophosphate, which is not as good in preventing corrosion and also may cause issues with forming calcium phosphate scale. When the combination of AAP,HPA, and HEDP (or another phosphonic acid) is used as a corrosion inhibitor according to a preferred embodiment of the invention, virtually no reversion of organic phosphate to orthophosphate was detected. Samples from composition Example Nos. 2 and 3 and comparative Example No. 7 were tested for the presence of orthophosphates upon mixing of the composition and again after 48 hours. The results are listed below in Table 5. Example Nos. 2 and 3, which use AAP, HPA, and HEDP (and contain AA/AMPS and TTA as noted above), showed very little orthophosphate increase over the 48 hour period, but comparative Example No. 7 which contains HPA and HEDP (and contains AA/AMPS and TTA as noted above), but no AAP, showed a substantial increase.

Table 5. Orthophosphate levels in low hardness test water in presence of biocide during the spinner corrosion test

	Orthophosphate (ppm PO4)	
Test	Initial	48hr (End of Test)
Example 2	0.4	0.5
Example 3	0.2	0.4
Comp. Ex -7	0.3	1.6

[0025] According to another preferred embodiment, a water treatment composition as listed in Table 6 (which is the same as Ex. 2 tested above) is effective at inhibiting corrosion in a water system over a broad range of LSI values and in the presence of a biocide.

Table 6.

Component	**Available as**	**Wt %**	**Active %* in Composition**
Sodium polyasparte (AAP)	Baypure DS100	13.0	5.2% as AAP
Hydroxy phosphonoacetic Acid (HPA)	Belcor 575	10.0	5.0% as HPA

(continued)

Component	Available as	Wt %	Active %* in Composition
1-Hydroxyethylidene 1,1-diphosphonic acid (HEDP)	Dequest 2010	5.25	3.0% as PO4
Monoethanolamine (MEA)	Monoethanolamine	1.0	0.99%
Copolymer of acrylic acid and sulfonated monomer (AA/AMPS)	NC-233	8.78	3.9% as AA/AMPS
Tolyltriazole (TTA)	Wintrol T50NA	9.40	4.0% as TTA
1,3,6,8-Pyrenetetrasulfonic acid tetrasodium salt (PTSA)	Spectra Trace SH-L 10%	1.00	1% as PTSA
	NaOH or KOH	15.00	N/A
Deionized water	Deionized water	36.57	N/A
*Active % refers to active weight percent. Wt% is raw material weight percent. Most of the raw materials are aqueous solutions and contain only a certain amount of solids that is the actual chemical component. The amount of active (Active %) is calculated based on raw material weight percent and the amount of the chemical in the solution per the information provided by the supplier. For example, Baypure DS100 is a 40% solution of AAP in water, so if we use 13% of Baypure we have: 0.13*0.40*100% = 5.2% of AAP (actual chemical) in the formula			

[0026] NaOH and/or KOH is preferably also added to the composition according to an embodiment of the invention. These ingredients are typically added to water treatment formulations in order to neutralize acid and to bring the pH of the final composition to the desired level. Most of the compositions will have pH > 8, some will have pH > 12. In compositions where TTA is used (as with a preferred embodiment of a composition according to the invention) it is desirable to have higher pH (> 11) for the composition in order to ensure solubility of TTA, which has very poor solubility at lower pH.

[0027] Additional spinner tests in low LSI water were carried out in order to test the effectiveness of various concentrations of treatment compositions for inhibiting corrosion according to preferred embodiments of the invention. The same spinner test parameters and low LSI water (Table 1) described above were used for these tests. The concentrations of the ingredients when added to the spinner test water and the results of these tests are shown below in Table 7. Figure 3 shows photographs of the test coupons (tested at a flow rate of 0.91 m/sec (3 ft/sec)) for each composition after the test was completed.

Table 7 - Additional Spinner Test Compositions & Results

Inhibitor	Unit	Comp. Ex. 10	Ex. 11	Ex. 12	Comp. Ex. 13	Ex. 14	Comp. Ex. 15	Ex. 16	Comp. Ex. 17
AAP	ppm active	2.6	5.2	7.8	5.0	10	10	5.0	5.0
HPA	ppm active	2.5	5.0	7.5	2.5	5	2.5	5.0	5.0
AAP:HPA Ratio		51:49	51:49	51:49	67:33	67:33	80:20	51:49	51:49
HEDP	ppm active	1.6 (1.5 ppm PO_4)	3.26 (3 ppm PO_4)	4.7 (4.4 ppm PO_4)	3.26 (3 ppm PO_4)	3.26 (3 ppm PO_4)	3.26 (3 ppm PO_4)		
PBTC	ppm active							2.6 (0.95 ppm PO_4)	
MEA	ppm				0.5	1	0.5		
TTA	ppm TTA	4	4	4	4	4	4	4	4
AA/AMPS Copolymer	ppm active	4	4	4	4	4	4	4	4

(continued)

Inhibitor	Unit	Comp. Ex. 10	Ex. 11	Ex. 12	Comp. Ex. 13	Ex. 14	Comp. Ex. 15	Ex. 16	Comp. Ex. 17
Corrosion Results from Spinner Test (low LSI water), mild steel (C1010) coupons at 0.91 m/sec (3ft/sec) flow rate									
Corrosion Rate*	mm/yr (MPY (mil/yr))	0.13 (5.2)	0.06 (2.3)	0.04 (1.5)	0.08 (3.1)	0.06 (2.2)	0.09 (3.5)	0.05 (2.1)	0.08 (3.3)
Pitting		Pitting	none	none	none	none	none	none	None
* Average for 2 coupons from the same spinner test pot at 0.91 m/sec (3 ft/sec)									

[0028] Comparative Examples 10, 13, and 15 use AAP, HPA, and HEDP but in amounts less than the preferred concentrations. These examples show increased corrosion (and Comp. Ex. 10 showed moderate pitting) at low levels of the inhibitors. Example Nos. 11-12, 14, and 16 according to preferred embodiments of the invention show good performance (low corrosion rate and no pitting) for different optional components and varying concentrations and ratios of AAP to HPA. The examples also show that the change from HEDP to PBTC (Ex. 16) and reduction of secondary chelates does not affect the corrosion inhibition performance of compositions according to preferred embodiments of the invention. Example No. 17 used AAP and HPA, without a second phosphonic acid, similar to the composition described in the ’023 patent. It shows improved results in controlling corrosion in low LSI water, but the results are not as good as in the examples according to preferred embodiments of the invention.

[0029] Additional spinner tests were conducted to compare compositions using AAP and PBTC as disclosed in the ’023 patent with compositions according to preferred embodiments of the invention. The test set-up was the same as described above using low LSI water, mild steel (C1010) coupons, and a flow rate of 0.91 m/sec (3 ft/sec). The results are shown in Table 8 below.

Table 8 - Comparing Compositons Using One Phosphonic Acid to Compositions Using Two Phosphonic Acids

Inhibitor	Unit	Comp. Example 18 80:20 PBTC/AAP	Comp. Example 19 40:60 PBTC/AAP	Example 20	Example 21	Example 12 (same as in Table 7)
PBTC	ppm active	16	8	4.8	8	
HEDP	ppm active					4.7
AAP	ppm active	4	12	7.8	4	7.8
HPA	ppm active			7.5	8	7.5
TTA	ppm TTA	4	4	4	4	4
AA/AMPS Copolymer	ppm active	4	4	4	4	4
Corrosion Rate*	mm/yr (MPY (mil/yr))	0.08 (3.1)	0.08 (3.1)	0.05 (1.9)	0.04 (1.7)	0.04 (1.5)
Pitting		none	none	none	None	None
*Average for 2 coupons from the same pot at 0.91 m/sec (3 ft/sec)						

[0030] As can be seen, the examples according to preferred embodiments of the invention (Example Nos. 20, 21, and 12) with AAP, HPA, and a second phosphonic acid (HEDP or PBTC) show much beter corrosion inhibition results than the comparatve examples using only AAP and PBTC (without any HPA). It is also noted that Comp. Ex. Nos. 18-19 resulted in corrosion rates greater than 0.07 mm/yr (3 MPY) even when using 20 ppm total inhibitor (AAP and PBTC), which is higher than the corrosion rate achievable with preferred compositions according to the invention using substantially less total inhibitor, such as Example No. 11, which had a corrosion rate of 0.06 mm/yr (2.3 MPY) using only 13.5 ppm total inhibitors (AAP, HPA, HEDP), and Example No. 16, which had a corrosion rate of 0.05 mm/yr (2.1 MPY) using only 12.6 ppm total inhibitors (AAP, HPA, PBTC). Additionally, the corrosion rates of Comp. Ex. Nos. 18-19 are comparable to those in Comp. Ex. Nos. 13 and 15, which use AAP, HPA, and a second phosphonic acid, but the total amount of inhibitor needed to achieve the results in Comp. Ex. Nos. 18-19 (20 ppm total) is much higher than that needed in Nos. 13 and 15 (10.76 and

15.76 ppm total, respectively). The results of these experiments show that the addition of a second phosphonic acid, in combination with AAP and HPA, provides an unexpected synergistic effect that improves corrosion inhibition even when less total inhibitor is used and even in the presence of a biocide.

[0031] Compositions according to the embodiments of the invention are effective in inhibiting corrosion on metal components in water systems over a broad range of LSI values, including LSI <0, and without requiring the use of regulated toxic metals. These compositions are also effective at higher pH values (7-9) typically found in water systems, such as cooling towers and boilers, whereas some prior art inhibitors are ineffective or their effectiveness is reduced at such pH levels (for example, a polyaspartic acid/stannous salt treatment is effective only at pH 5-7). These compositions according to the invention also prevent reversion of organic phosphate to orthophosphate to maintain effectiveness in the presence of a biocide.

[0032] Other experiments using an electrochemical method were conducted to test compositions according to the invention for white rust prevention. The results in Table 9 below show synergistic effect of combining HPA and AAP (without another phosphonic acid) in reducing white rust formation as compared to use of each individual component (HPA alone and AAP alone). The cyclic voltammetry test was conducted in 0.1M sodium carbonate solution using zinc electrode. The measure of oxidation is the area under the oxidation curve peak observed; the lower the area the less oxidation occurs, meaning lower corrosion rate. The results are the averages of 6-10 experiments with standard deviation.

Table 9

Inhibitor	Concentration [ppm active]	Measure of Oxidation [Coulombs*10^{-3}]
AAP	50	1.2 ± 0.2
HPA	50	1.0 ± 0.1
AAP/HPA (1:1 ratio)	25 : 25	0.8 ± 0.1

[0033] Additional spinner corrosion tests were carried out in stainless steel containers in high alkalinity water known to form white rust on galvanized surfaces to test the effectiveness of compositions according to preferred embodiments of the invention for the prevention of white rust formation. The water chemistry, characteristic of high alkalinity synthetic water, in these tests is detailed in Table 10 below. Four Hot Dip Galvanized steel coupons (HDG G70) with dimensions 1.0x4.0x0.02in were installed in each container on the holders hanging from a rotating shaft that rotates at 147 rotations/min that represents flow rate of 0.91-1.52 m/s (3-5 ft/s), depending on coupon distance from center of the rotating shaft. During the tests the water was aerated and maintained at constant temperature of 49°C (120F) and constant volume (any evaporation was compensated with automatic addition of DI water when the water level dropped below a sensor level). Standard test duration was 48 hours. The active ingredients used in two comparative examples and three examples of preferred compositions according to the invention, along with corrosion rates, are listed in Table 11.

Table 10 - High alkalinity/no hardness water used in Spinner test experiments for white rust prevention

Characteristic	Value	Unit
pH	8.7-8.9	
Conductivity	2300	cP
Ca Hardness	0	ppm, (as $CaCO_3$)
Mg Hardness	0	ppm, (as $CaCO_3$)
Chlorides, Total	250	ppm Cl
M Alkalinity	200	ppm, (as $CaCO_3$)
Sulfate, Total	500	ppm, as SO_4

Table 11 - Active Ingredients Composition and Galvanized Coupon Corrosion Rate

Inhibitor	Unit	Comp. Ex. 22 - No Inhibitor	Comp. Ex. 23	Ex. 24	Ex. 25	Ex. 26
AAP	ppm active	-	-	15	7.5	15
HPA	ppm active	-	7.5	7.5	2.5	-

(continued)

Inhibitor	Unit	Comp. Ex. 22 - No Inhibitor	Comp. Ex. 23	Ex. 24	Ex. 25	Ex. 26
HEDP	ppm active	-	3.26 (3 ppm PO_4)	3.26 (3 ppm PO_4)	3.26 (3 ppm PO_4)	3.26 (3 ppm PO_4)
TTA	ppm TTA	-	4	4	4	4
AA/AMPS Co-polym er	ppm active	-	4	4	4	4
Corrosion Results- Galvanized Coupons (HDG G70)						
Corrosion Rate*	mm/yr (MPY (mil/yr))	1.36 (53.7)	0.61 (24.3)	0.25 (9.9)	0.36 (14.0)	0.27 (10.7)
*Average for 4 coupons from the same pot (two at 0.91 m/sec (3 ft/sec) and two at 1.52 m/sec (5 ft/sec) flow rate)						

[0034] In order to calculate the corrosion rate using the weight loss method, the galvanized coupons from these tests were cleaned according to standard procedure by immersing coupons in concentrated ammonium acetate and rinsing. FIG. 4 shows photographs of the galvanized coupons after the spinner tests with the compositions described in Table 12, both before and after cleaning. The white deposit visible on the coupons before cleaning is white rust. The damage of the galvanized layer due to corrosion, shown as dark spots, is visible on the coupons after cleaning. The blank (Comp. Ex. 22 - No Treatment) coupon was completely covered in white deposit and after cleaning most of the galvanized layer was removed with visible mild steel corrosion. The coupon treated with HPA and HEDP without an amino-acid based polymer (Comp. Ex. 23) showed substantial white rust formation, but was still a great improvement over the control (Comp. Ex. 22). Significantly better results were obtained with compositions in Examples 24-26. The best results were achieved with Ex. 24 using AAP, HPA at greater than 3 ppm, and a second phosphonic acid (HEDP). Although the use of HPA is important in inhibiting mild steel corrosion, its use is optional for white rust treatment. As can be seen from Example 26, the results of using AAP and HEDP without HPA were almost as good as the three combined. Accordingly, a preferred composition for treating white rust according to the invention comprises 2-15% amino-acid based polymer, 0-10% HPA, and 0-10% of a second phosphonic acid. Preferably, the amount of active amino-acid based polymer in a treatment composition according to the invention is at least 3ppm, more preferably 3 ppm - 50 ppm, and most preferably 5 ppm - 30 ppm, all as concentrations when added to the volume of water in the water system being treated. More preferably, the AAP is used in conjunction with HPA in an amount of at least 3 ppm, more preferably from 3 ppm - 50 ppm, and most preferably from 3 ppm - 20 ppm and/or another phosphonic acid in an amount of at least 2 ppm more preferably from 2 ppm- 20 ppm, and most preferably from 2 ppm - 10 ppm.

[0035] For treating white rust according to the invention, it is preferred to use both hydroxyphosphonoacetic acid and an amino-acid based polymer, and more preferably in conjunction with a second phosphonic acid, in the weight range amounts indicated above, but it has also been found that the use of an amino-acid based polymer or hydroxyphosphonoacetic without the other is beneficial at inhibiting white rust.

[0036] According to one preferred method of preventing corrosion of metal components and/or white rust on galvanized steel components in a water system, a treatment composition according to the invention as described above is added to the water system at a preferred effective feed rate of 20ppm - 600 ppm, or more preferably 100 - 300ppm, of treatment composition depending on the treated water chemistry and the amount of optional components in the treatment composition. Preferably, a sufficient amount of treatment composition is added to the water system to provide effective active amounts of AAP of at least 3 ppm and of HPA of at least 3 ppm, both as concentrations when added to the volume of water in the water system being treated. More preferably, the amount of HPA is at least 3 ppm. More preferably, the treatment composition is added in a sufficient amount to provide effective active amounts of AAP between 3 ppm - 50 ppm, HPA between 3ppm - 50 ppm, and a second phosphonic acid between 2 ppm - 20 ppm when added to the water in the water system. Most preferably, these effective active amounts are 5ppm - 30 ppm AAP, 3 ppm - 20 ppm HPA, and a second phosphonic acid between 2ppm - 10 ppm when added to the water in the water system. For treating white rust, the use of HPA is optional, so the treatment composition used in a preferred method according to the invention may comprise AAP without any HPA and be added in amounts sufficient to provide these same concentration ranges of AAP in the water of the water system being treated. According to another preferred embodiment, the composition added to the water system comprises a fluorescent tracer so that the level of composition in the water system can be measured and monitored. Additional treatment composition is added to the water system as needed, based on the tracer measurements, to maintain an effective amount of treatment within the water system.

[0037] All ppm concentrations of the various treatments in the example tests described herein are concentrations when added to the water in the spinner test, to correlate to the concentrations when added to the water in the water system being treated. Unless specifically excluded, all references to acids herein and in the claims include water soluble salts of the acid, as will be understood by those of ordinary skill in the art.

Claims

1. A method of treating a water system to inhibit corrosion or white rust formation on metal components in the water system, the method comprising adding to the water system having a volume of water:

   an amino-acid based polymer or its water soluble salt; a first phosphonic acid or its water soluble salt; and a second phosphonic acid or its water soluble salt; and
   wherein the first phosphonic acid is hydroxyphosphonoacetic acid or its water soluble salt;
   wherein the adding step provides an active concentration in the volume of water of (1) 3 ppm - 50 ppm of the amino-acid based polymer or its water soluble salt, (2) 3 ppm - 50 ppm ppm of the hydroxyphosphonoacetic acid or its water soluble salt, and (3) 2 ppm - 20 ppm of the second phosphonic acid or its water soluble salt; and
   wherein no zinc, chromate, molybdate, or tin are added to the water in the water system.

2. The method of claim 1 wherein the amino-acid based polymer is polyaspartic acid or a salt thereof.

3. The method of claim 1 or claim 2 wherein the adding step provides an active concentration of (1) 5 ppm - 30 ppm of the amino-acid based polymer or its water soluble salt,(2) 3 ppm - 20 ppm of the hydroxyphosphonoacetic acid or its water soluble, and (3) 2 ppm - 10 ppm of the second phosphonic acid or its water soluble salt.

4. The method of claim 1 or claim 2 wherein the adding step provides a combined active concentration of the amino-acid based polymer or its water soluble salt, hydroxyphosphonoacetic acid or its water soluble salt, and other phosphonic acid or its water soluble salt of at least 9 ppm in the volume of water in the water system.

5. The method of any one of claims 1-3 wherein the amino-acid based polymer or its water soluble salt, first phosphonic acid or its water soluble salt, and second phosphonic acid or its water soluble salt are combined in a treatment composition prior to the adding step and wherein the treatment composition comprises 2%-15% by weight of the amino-acid based polymer or its water soluble salt, 2% to 10% by weight of the first phosphonic acid or ist water soluble salt, and 2% bis 10% by weight of the second phosphonic acid or its water soluble salt.

6. The method of claim 5 wherein the treatment composition further comprises a tracer and wherein the method further comprises periodically measuring an amount of the treatment composition in the water system based on a measurement of the tracer.

7. The method of claim 6 wherein the treatment composition further comprises one or more of a neutralizing amine, chlorine stabilizer, a scale inhibitor, a dispersion agent, another corrosion inhibitor, chelants, and an azole corrosion inhibitor.

8. The method of any one of claims 1-4 wherein the second phosphonic acid is HEDP.

9. The method of any one of claims 1-4 wherein the second phosphonic acid is a phosphonocarboxylic acid.

10. The method of claim 9 wherein the phosphonocarboxylic acid is PBTC.

11. The method of any of the preceding claims further comprising adding one or more of a neutralizing amine, chlorine stabilizer, a scale inhibitor, a dispersion agent, another corrosion inhibitor, chelants, an azole corrosion inhibitor, and a fluorescent dye tracer to the water in the water system.

12. A composition for inhibiting corrosion or white rust on metal components in water systems comprising a volume of water, the composition comprising:

    2-15% by weight of an amino-acid based polymer or its water soluble salt;
    2-10% by weight of hydroxyphosphonoacetic acid or its water soluble salt;
    2-10% by weight of a second phosphonic acid or its water soluble salt; and

one or more of a neutralizing amine, chlorine stabilizer, a scale inhibitor, a dispersion agent, another corrosion inhibitor, chelants, an azole corrosion inhibitor, and a fluorescent dye tracer; and
wherein the composition does not include zinc, chromate, molybdate or tin.

13. The composition according to claim 12 wherein (1) the second phosphonic acid is PBTC or HEDP and (2) the amino-acid based polymer is polyaspartic acid or a salt thereof.

14. The composition according to any of claims 12-13 wherein the amino-acid based polymer is sodium polyaspartate.

15. The composition according to claim 12 wherein the second phosphonic acid is a phosphonocarboxylic acid and a weight ratio of the amino-acid based polymer or its water soluble salt to hydroxyphosphonoacetic acid or its water soluble salt is in a range of 90:10 to 10:90 and a weight ratio of the amino-acid based polymer or its water soluble salt and the hydroxyphosphonoacetic acid or its water soluble salt combined to the phosphonocarboxylic acid or its water soluble salt is in a range of 90:10 to 60:40.

16. The composition according to any one of claims 12-14 further comprising one or more monoethanol amine, a polycarboxylate polymer, a carboxylate/sulfonate functional copolymer, benzotriazole, alkylbenzotriazole (tolyltriazole), and 1,3,6,8-Pyrenetetrasulfonic acid tetrasodium salt.

17. The composition according to any one of claims 12-16 wherein the composition comprises (1) an amount of the amino-acid based polymer or its water soluble salt and hydroxyphosphonoacetic acid or its water soluble salt sufficient to yield an active concentration of 3 ppm - 50 ppm of the amino-acid based polymer or its water soluble salt, (2) (2) an amount of the hydroxyphosphonoacetic acid or its water soluble salt sufficient to yield an active concentration of 3 ppm - 50 ppm , and (3) an amount of the second phosphonic acid or its water soluble salt sufficient to yield an active concentration of 2 ppm - 20ppm when added to a volume of water in the water system.

18. The composition according to any one of claims 12-14 wherein the composition comprises an amount of polyaspartic acid or a salt thereof and hydroxyphosphonoacetic acid or its water soluble salt sufficient to yield at least 3 ppm active amino-acid based polymer and at least 3 ppm active hydroxyphosphonoacetic acid when added to a volume of water in the water system.

19. The composition according to any one of claims 12-14 wherein the second phosphonic acid is HEDP or its water soluble salt.

20. The method of any one of claims 1 or 8-10, wherein the water in the water system contains a biocide and/or has a pH greater than 7.

21. The method of any one of claims 1-12 or 20, wherein the water system is a cooling tower.

Patentansprüche

1. Verfahren zur Behandlung eines Wassersystems zur Verhinderung von Korrosion oder Weißrostbildung auf Metallkomponenten in dem Wassersystem, wobei das Verfahren die Zugabe eines Wasservolumens zu dem Wassersystem umfasst:

ein Polymer auf Aminosäurebasis oder sein wasserlösliches Salz; eine erste Phosphonsäure oder ihr wasserlösliches Salz; und
eine zweite Phosphonsäure oder ihr wasserlösliches Salz; und
wobei die erste Phosphonsäure Hydroxyphosphonoessigsäure oder ihr wasserlösliches Salz ist;
wobei der Zugabeschritt eine aktive Konzentration in dem Wasservolumen von (1) 3 ppm - 50 ppm des Polymers auf Aminosäurebasis oder seines wasserlöslichen Salzes, (2) 3 ppm - 50 ppm der Hydroxyphosphonoessigsäure oder ihres wasserlöslichen Salzes und (3) 2 ppm - 20 ppm der zweiten Phosphonsäure oder ihres wasserlöslichen Salzes bereitstellt; und
wobei dem Wasser im Wassersystem kein Zink, Chromat, Molybdat oder Zinn zugesetzt wird.

2. Verfahren nach Anspruch 1, wobei das Polymer auf Aminosäurebasis Polyasparaginsäure oder ein Salz davon ist.

3. Verfahren nach Anspruch 1 oder Anspruch 2, wobei der Zugabeschritt eine aktive Konzentration von (1) 5 ppm - 30 ppm des Polymers auf Aminosäurebasis oder seines wasserlöslichen Salzes, (2) 3 ppm - 20 ppm der Hydroxyphosphonoessigsäure oder ihres wasserlöslichen Salzes und (3) 2 ppm - 10 ppm der zweiten Phosphonsäure oder ihres wasserlöslichen Salzes bereitstellt.

4. Verfahren nach Anspruch 1 oder Anspruch 2, wobei der Zugabeschritt eine kombinierte aktive Konzentration des Polymers auf Aminosäurebasis oder seines wasserlöslichen Salzes, der Hydroxyphosphonoessigsäure oder ihres wasserlöslichen Salzes und anderer Phosphonsäure oder ihres wasserlöslichen Salzes von mindestens 9 ppm im Wasservolumen im Wassersystem bereitstellt.

5. Verfahren nach einem der Ansprüche 1 bis 3, wobei das Polymer auf Aminosäurebasis oder sein wasserlösliches Salz, die erste Phosphonsäure oder ihr wasserlösliches Salz und die zweite Phosphonsäure oder ihr wasserlösliches Salz vor dem Zugabeschritt in einer Behandlungszusammensetzung kombiniert werden und wobei die Behandlungszusammensetzung 2 bis 15 Gew.-% des Polymers auf Aminosäurebasis oder seines wasserlöslichen Salzes, 2 bis 10 Gew.-% der ersten Phosphonsäure oder ihres wasserlöslichen Salzes und 2 bis 10 Gew.-% der zweiten Phosphonsäure oder ihres wasserlöslichen Salzes umfasst.

6. Verfahren nach Anspruch 5, wobei die Behandlungszusammensetzung ferner einen Tracer umfasst und wobei das Verfahren ferner das periodische Messen einer Menge der Behandlungszusammensetzung in dem Wassersystem auf der Grundlage einer Messung des Tracers umfasst.

7. Verfahren nach Anspruch 6, wobei die Behandlungszusammensetzung ferner eines oder mehrere von einem neutralisierenden Amin, Chlorstabilisator, einem Kesselsteininhibitor, einem Dispersionsmittel, einem weiteren Korrosionsinhibitor, Chelatbildnern und einem Azol-Korrosionsinhibitor enthält.

8. Verfahren nach einem der Ansprüche 1 bis 4, wobei die zweite Phosphonsäure HEDP ist.

9. Verfahren nach einem der Ansprüche 1 bis 4, wobei die zweite Phosphonsäure eine Phosphonocarbonsäure ist.

10. Verfahren nach Anspruch 9, wobei die Phosphonocarbonsäure PBTC ist.

11. Verfahren nach einem der vorhergehenden Ansprüche ferner umfassend die Zugabe eines oder mehrerer von einem neutralisierenden Amin, Chlorstabilisator, einem Kesselsteininhibitor, einem Dispersionsmittel, einem weiteren Korrosionsinhibitor, Chelatbildnern, einem Azol-Korrosionsinhibitor und einem Fluoreszenzfarbstoff-Tracer zum Wasser im Wassersystem.

12. Zusammensetzung zur Verhinderung von Korrosion oder Weißrost auf Metallkomponenten in Wassersystemen, die ein Wasservolumen umfassen, wobei die Zusammensetzung umfasst:

2-15 Gew.-% eines Polymers auf Aminosäurebasis oder seines wasserlöslichen Salzes;
2-10 Gew.-% Hydroxyphosphonoessigsäure oder ihres wasserlösliches Salz
2-10 Gew.-% einer zweiten Phosphonsäure oder ihres wasserlöslichen Salzes; und
eines oder mehrere von einem neutralisierenden Amin, Chlorstabilisator, einem Kesselsteininhibitor, einem Dispersionsmittel, einem weiteren Korrosionsinhibitor, Chelatbildnern, einem Azol-Korrosionsinhibitor und einem Fluoreszenzfarbstoff-Tracer; und
wobei die Zusammensetzung kein Zink, Chromat, Molybdat oder Zinn enthält.

13. Zusammensetzung nach Anspruch 12, wobei (1) die zweite Phosphonsäure PBTC oder HEDP ist und (2) das Polymer auf Aminosäurebasis Polyasparaginsäure oder ein Salz davon ist.

14. Zusammensetzung nach einem der Ansprüche 12 bis 13, wobei das Polymer auf Aminosäurebasis Natriumpolyaspartat ist.

15. Zusammensetzung nach Anspruch 12, wobei die zweite Phosphonsäure eine Phosphonocarbonsäure ist und das Gewichtsverhältnis des Polymers auf Aminosäurebasis oder seines wasserlöslichen Salzes zur Hydroxyphosphonoessigsäure oder ihres wasserlöslichen Salzes im Bereich von 90:10 bis 10:90 liegt und das Gewichtsverhältnis des Polymers auf Aminosäurebasis oder seines wasserlöslichen Salzes und der Hydroxyphosphonoessigsäure oder ihres wasserlöslichen Salzes in Kombination mit der Phosphonocarbonsäure oder ihres wasserlöslichen Salzes im

Bereich von 90:10 bis 60:40 liegt.

16. Zusammensetzung nach einem der Ansprüche 12 bis 14, ferner umfassend ein oder mehrere Monoethanolamin, ein Polycarboxylatpolymer, ein Carboxylat/Sulfonat-funktionelles Copolymer, Benzotriazol, Alkylbenzotriazol (Tolyltriazol) und 1,3,6,8-Pyrentetrasulfonsäure-Tetranatriumsalz.

17. Zusammensetzung nach einem der Ansprüche 12 bis 16, wobei die Zusammensetzung (1) eine Menge des Polymers auf Aminosäurebasis oder seines wasserlöslichen Salzes und der Hydroxyphosphonoessigsäure oder ihres wasserlöslichen Salzes, die ausreicht, um eine aktive Konzentration von 3 ppm - 50 ppm des Polymers auf Aminosäurebasis oder seines wasserlöslichen Salzes zu ergeben, (2) eine Menge der Hydroxyphosphonoessigsäure oder ihres wasserlöslichen Salzes, die ausreicht, um eine aktive Konzentration von 3 ppm - 50 ppm zu ergeben, und (3) eine Menge der zweiten Phosphonsäure oder ihres wasserlöslichen Salzes, die ausreicht, um eine aktive Konzentration von 2 ppm - 20 ppm zu ergeben, umfasst, wenn sie zu einem Wasservolumen in dem Wassersystem gegeben wird.

18. Zusammensetzung nach einem der Ansprüche 12 bis 14, wobei die Zusammensetzung eine Menge an Polyasparaginsäure oder einem Salz davon und Hydroxyphosphonoessigsäure oder ihrem wasserlöslichen Salz umfasst, die ausreicht, um mindestens 3 ppm aktives Polymer auf Aminosäurebasis und mindestens 3 ppm aktive Hydroxyphosphonoessigsäure zu ergeben, wenn sie zu einem Wasservolumen in dem Wassersystem gegeben wird.

19. Zusammensetzung nach einem der Ansprüche 12 bis 14, wobei die zweite Phosphonsäure HEDP oder ihr wasserlösliches Salz ist.

20. Verfahren nach einem der Ansprüche 1 oder 8 bis 10, wobei das Wasser im Wassersystem ein Biozid enthält und/oder einen pH-Wert von mehr als 7 aufweist.

21. Verfahren nach einem der Ansprüche 1 bis 12 oder 20, wobei das Wassersystem ein Kühlturm ist.

Revendications

1. Procédé de traitement d'un circuit d'eau afin d'inhiber la corrosion ou la formation de rouille blanche sur des composants métalliques du circuit d'eau, le procédé comprenant l'ajout, au circuit d'eau comportant un volume d'eau :

un polymère à base d'acide aminé ou son sel hydrosoluble ; un premier acide phosphonique ou son sel hydrosoluble ; et
un second acide phosphonique ou son sel hydrosoluble ; et
dans lequel le premier acide phosphonique est l'acide hydroxyphosphonoacétique ou son sel hydrosoluble ;
dans lequel l'étape d'ajout fournit une concentration active dans le volume d'eau de (1) 3 ppm à 50 ppm du polymère à base d'acide aminé ou de son sel hydrosoluble, (2) 3 ppm à 50 ppm de l'acide hydroxyphosphonoacétique ou de son sel hydrosoluble, et (3) 2 ppm à 20 ppm du second acide phosphonique ou de son sel hydrosoluble ; et
dans lequel ni zinc, ni chromate, ni molybdate, ni étain ne sont ajoutés dans le circuit d'eau.

2. Procédé selon la revendication 1 dans lequel le polymère à base d'acide aminé est un acide polyaspartique ou un sel de celui-ci.

3. Procédé selon la revendication 1 ou la revendication 2 dans lequel l'étape d'ajout fournit une concentration active de (1) 5 ppm à 30 ppm du polymère à base d'acide aminé ou de son sel hydrosoluble, (2) 3 ppm à 20 ppm de l'acide hydroxyphosphonoacétique ou de son sel hydrosoluble, et (3) 2 ppm à 10 ppm du second acide phosphonique ou de son sel hydrosoluble.

4. Procédé selon la revendication 1 ou la revendication 2 dans lequel l'étape d'ajout fournit une concentration active combinée du polymère à base d'acide aminé ou de son sel hydrosoluble, de l'acide hydroxyphosphonoacétique ou de son sel hydrosoluble et de l'autre acide phosphonique ou de son sel hydrosoluble d'au moins 9 ppm dans le volume d'eau dans le circuit d'eau.

5. Procédé selon l'une quelconque des revendications 1 à 3 dans lequel le polymère à base d'acide aminé ou son sel hydrosoluble, le premier acide phosphonique ou son sel hydrosoluble et le second acide phosphonique ou son sel hydrosoluble sont combinés dans une composition de traitement avant l'étape d'ajout et dans lequel la composition de traitement comprend de 2 % à 15 % en poids combinée du polymère à base d'acide aminé ou de son sel hydrosoluble, de 2 % à 10 % en poids du premier acide phosphonique ou de son sel hydrosoluble et de 2 % à 10 % en poids du second acide phosphonique ou de son sel hydrosoluble.

6. Procédé selon la revendication 5 dans lequel la composition de traitement comporte, en outre, un traceur et dans lequel le procédé comprend, en outre, le mesurage périodique d'une quantité de la composition de traitement dans le circuit d'eau sur la base d'un mesurage du traceur.

7. Procédé selon la revendication 6, dans lequel la composition de traitement comporte un outre un ou plusieurs agents parmi une amine neutralisante, un stabilisateur de chlore, un antitartre, un dispersant, un autre inhibiteur de corrosion, des chélateurs et un inhibiteur de corrosion azole.

8. Procédé selon l'une quelconque des revendications 1 à 4 dans lequel le second acide phosphonique est le HEDP.

9. Procédé selon l'une quelconque des revendications 1 à 4 dans lequel le second acide phosphonique est un acide phosphonocarboxylique.

10. Procédé selon la revendication 9 dans lequel l'acide phosphonocarboxylique est le PBTC.

11. Procédé selon l'une quelconque des revendications précédentes comprenant, en outre, l'ajout d'un ou plusieurs agents parmi une amine neutralisante, un stabilisateur de chlore, un antitartre, un dispersant, un autre inhibiteur de corrosion, des chélateurs, un inhibiteur de corrosion azole et un traceur coloré fluorescent dans l'eau du circuit d'eau.

12. Composition destinée à inhiber la corrosion ou la rouille blanche sur des composants métalliques dans des circuits d'eau comprenant un volume d'eau, la composition comprenant :

de 2 à 15 % en poids d'un polymère à base d'acide aminé ou de son sel hydrosoluble ;
de 2 à 10 % en poids d'acide hydroxyphosphonoacétique ou de son sel hydrosoluble ;
de 2 à 10 % en poids d'un second acide phosphonique ou de son sel hydrosoluble ; et
un ou plusieurs agents parmi une amine neutralisante, un stabilisateur de chlore, un antitartre, un dispersant, un autre inhibiteur de corrosion, des chélateurs, un inhibiteur de corrosion azole et un traceur coloré fluorescent ; et dans laquelle la composition ne comporte pas de zinc, de chromate, de molybdate ou d'étain.

13. Composition selon la revendication 12 dans laquelle (1) le second acide phosphonique est le PBTC ou le HEDP et (2) le polymère à base d'acide aminé est l'acide polyaspartique ou un sel de celui-ci.

14. Composition selon l'une quelconque des revendications 12 à 13 dans laquelle le polymère à base d'acide aminé est le polyaspartate de sodium.

15. Composition selon la revendication 12 dans laquelle le second acide phosphonique est un acide phosphonocarboxylique et un rapport pondéral du polymère à base d'acide aminé ou de son sel hydrosoluble à l'acide hydroxyphosphonoacétique ou à son sel hydrosoluble est dans une fourchette de 90:10 à 10:90 et un rapport pondéral du polymère à base d'acide aminé ou de son sel hydrosoluble et de l'acide hydroxyphosphonoacétique ou de son sel hydrosoluble combinés à l'acide phosphonocarboxylique ou à son sel hydrosoluble est dans une fourchette de 90:10 à 60:40.

16. Composition selon l'une quelconque des revendications 12 à 14 comprenant, en outre, un ou plusieurs composés parmi la monoéthanolamine, un polymère polycarboxylate, un copolymère fonctionnel carboxylate-sulfonate, le benzotriazole, un alkylbenzotriazole (tolyltriazole) et un sel tétrasodique d'acide 1,3,6,8-pyrènetétrasulfonique.

17. Composition selon l'une quelconque des revendications 12 à 16 dans laquelle la composition comprend (1) une quantité du polymère à base d'acide aminé ou de son sel hydrosoluble et de l'acide hydroxyphosphonoacétique ou de son sel hydrosoluble suffisante pour produire une concentration active de 3 ppm à 50 ppm du polymère à base d'acide aminé ou de son sel hydrosoluble, (2) une quantité de l'acide hydroxyphosphonoacétique ou de son sel hydrosoluble suffisante pour produire une concentration active de 3 ppm à 50 ppm et (3) une quantité du second acide phosphonique ou de son sel hydrosoluble suffisante pour produire une concentration active de 2 ppm à 20 ppm quand on les ajoute à un volume d'eau dans le circuit d'eau.

18. Composition selon l'une quelconque des revendications 12 à 14 dans laquelle la composition comprend une quantité d'acide polyaspartique ou d'un sel de celui-ci et d'acide hydroxyphosphonoacétique ou de son sel hydrosoluble suffisante pour produire au moins 3 ppm de polymère à base d'acide aminé actif et au moins 3 ppm d'acide hydroxyphosphonoacétique actif quand on les ajoute à un volume d'eau dans le circuit d'eau.

19. Composition selon l'une quelconque des revendications 12 à 14 dans laquelle le second acide phosphonique est le HEDP ou son sel hydrosoluble.

20. Procédé selon l'une quelconque des revendications 1 ou 8 à 10, dans lequel l'eau dans le circuit d'eau contient un biocide et/ou présente un pH supérieur à 7.

21. Procédé selon l'une quelconque des revendications 1 à 12 ou 20, dans lequel le circuit d'eau est une tour de refroidissement.

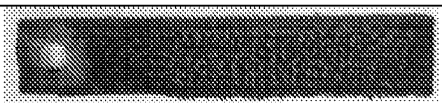
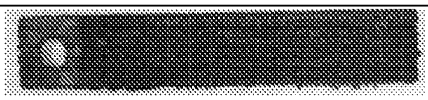
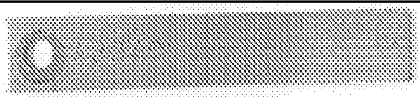
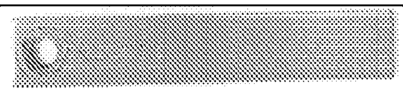
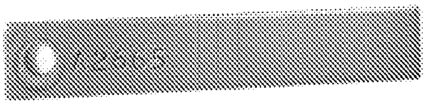
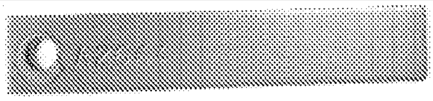
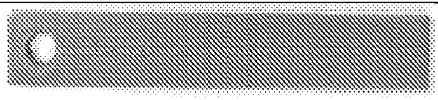
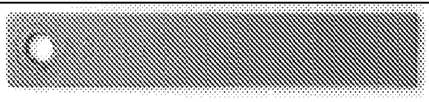
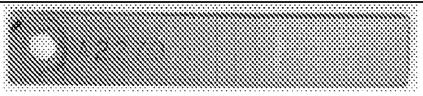
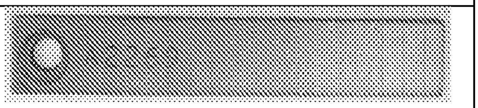
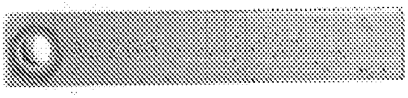
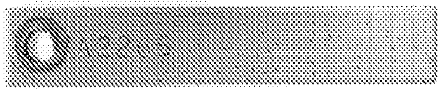
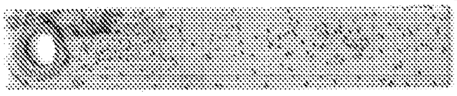
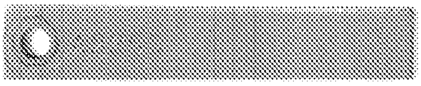
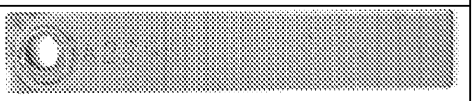
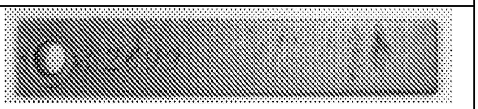
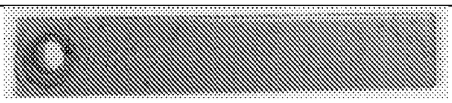
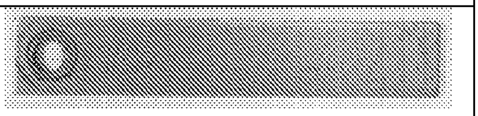
	Carbon Steel Coupon	
Test	Flow Rate = 3ft/sec	Flow rate = 5ft/sec
Control (no treatment)		
Example 1		
Example 2		
Example 3		
Comp. Ex.4		
Comp. Ex.5		
Comp. Ex.6		
Comp. Ex.7		
Comp. Ex.8		
Comp. Ex.9		

FIG. 1

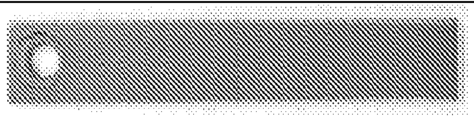
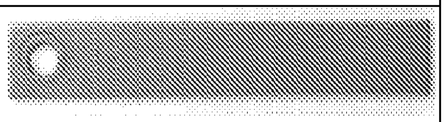
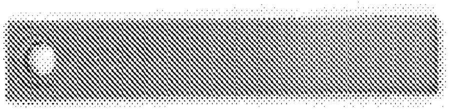
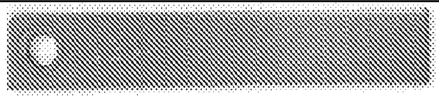
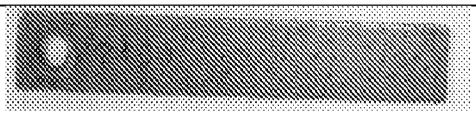
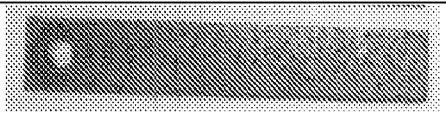
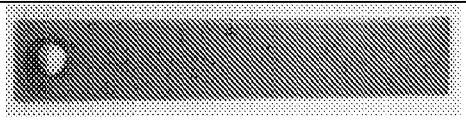
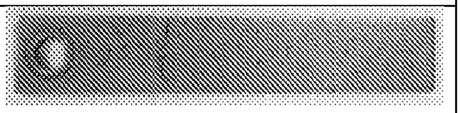
	Carbon Steel Coupon	
Test	Flow Rate = 3ft/sec	Flow rate = 5ft/sec
Example 2		
Example 3		
Comp. Ex.4		
Comp. Ex. 7		

FIG. 2

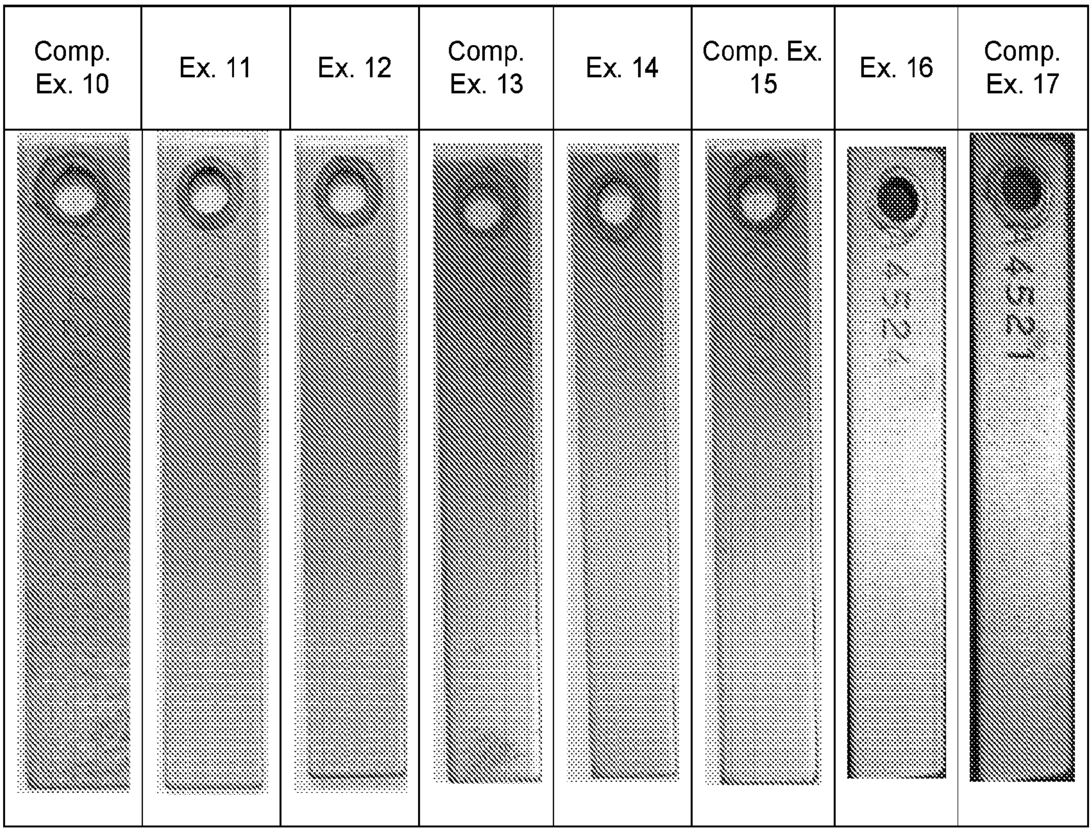


FIG. 3

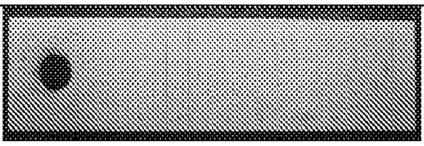
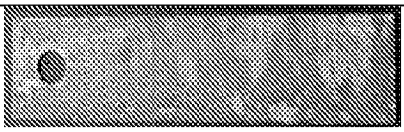
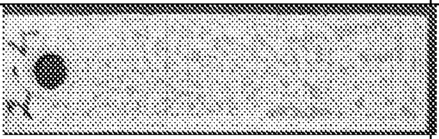
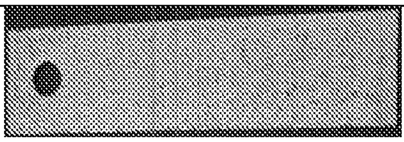
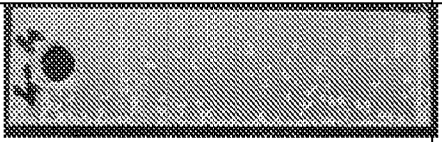
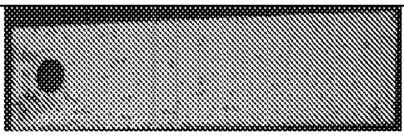
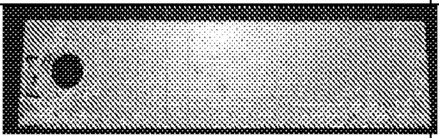
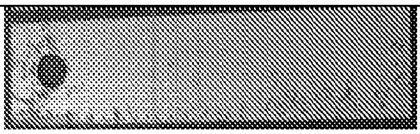
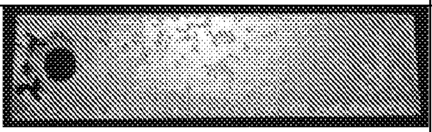
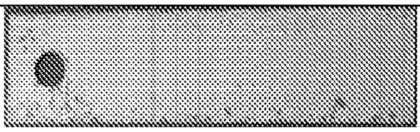
	Galvanized Coupon	
Test	Before Cleaning	After cleaning
Comp. Ex. 22 No Inhibitor		
Comp. Ex. 23		
Example 24		
Example 25		
Example 26		

FIG. 4

REFERENCES CITED IN THE DESCRIPTION

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- US 6468470 B **[0004] [0005]**
- US 6183649 B **[0004]**
- CN 103319010 **[0005]**
- CN 1273393 C **[0005]**
- CN 102838216 **[0005]**
- CN 1743282 **[0005]**